

RESULT OF HEATING A MIXTURE OF AMMONIUM NITRATE AND MANGANESE DIOXIDE.

JAMES H. RANSOM.

Practically all the work on catalysis, in which the oxides of the metals were the catalytic agents, has been undertaken with those substances which on heating decompose with the evolution of oxygen. It has been thought by some of those who have given the subject careful investigation that, in the case of manganese dioxide, at least, the reaction is one of alternate oxidation and reduction of the catalytic agent. The arguments are not conclusive, however, so that the question whether the manganese dioxide acts as a simple contact agent or takes a chemical part in the reaction remains unanswered.

It occurred to the writer to try the effect of catalytic agents on substances which, on heating, decompose without the formation of oxygen. It was thought that if the catalytic agent acted simply as a contact agent the temperature of decomposition would be lowered but the products would be the same as when the substance was heated alone; but if the action were chemical the products would be different, perhaps more or less oxidized than when the substance was heated by itself. It was recognized, however, that if the action followed the latter supposition it would not of necessity demonstrate that all so-called cases of catalysis were chemical. Among the substances easily available for such an experiment is ammonium nitrate, which, as is well known, decomposes quite smoothly into nitrous oxide and water. The temperature of decomposition is 205°.

At my suggestion, therefore, Mr. O. C. Haworth, who was then studying the effect of various catalytic agents, undertook the preliminary investigation of the effect of heating ammonium nitrate in the presence of different oxides, among them being manganese dioxide. He established the facts that the decomposition takes place at a lower temperature than when the nitrate is heated alone; that little if any oxygen or nitrous oxide is produced; that the gas evolved is nitrogen.

On consulting the literature it was found that in 1877 Gatehouse published a short note in the *Chemical News* giving the results of an experiment on heating a mixture of these substances. He observed that the gas was nitrogen, and from its volume he developed an equation to explain the reaction. According to him each molecule of the oxide reacts with four molecules of the nitrate; producing six atoms of nitrogen and a molecule of manganese nitrate. The presence of the last substance he does not seem to have confirmed; and as the temperature to which he heated the mixture was above that at which manganese nitrate decomposes it appeared doubtful that the final products were as he thought. The work begun by Mr. Haworth has been continued by the writer and the nature of the reaction made more nearly complete.

In our earlier experiments some difficulties were encountered and some facts observed which modified the procedure in the later work. First, it was found most difficult so to regulate the temperature that the reaction would go smoothly and in one direction. The action would proceed at about 200° until nearly one-half of the gas had been evolved, and then suddenly without apparent cause the thermometer would suddenly mount to 300° or more and brown gases be evolved in such quantities that the stopper and connections would be forced out with explosive violence. It was thought at first that manganese nitrate was being formed in the earlier stage of the reaction and later was decomposing with evolution of heat; but experiments with this substance showed that it decomposed in a regular manner between 130° and 185° . But by heating for a time to 210° - 220° and then cooling to 170° as the action proceeded it was found possible to regulate the decomposition and get consistent results.

It was also noted that after extracting the residue to determine the amount of soluble material the aqueous solution was very strongly acid with what appeared to be a nitrogen acid. The residue left on evaporation consisted of unchanged ammonium nitrate, and at times of a trace of a manganese compound.

In the succeeding experiments the apparatus was so modified that the gases could be passed through water to absorb the acid, and then collected in a large gas burette made with litre cylinders and filled with dilute alkali. About equal weights of ammonium nitrate and manganese dioxide were placed in a distilling flask connected with the acid absorbing bottle and the air in the apparatus replaced with nitrogen. The mixture was heated to 170° and then connected to the gas burette. Afterwards the

temperature was raised to between 220° and 230° and maintained there until the gas was about one-half evolved. The temperature was then lowered to 170° and kept there until the action was nearly complete, when it was again raised to 230° as long as a gas was being evolved. Finally it was cooled to 170° and the burette disconnected. Any oxygen in the burette was absorbed by pyrogallate (usually a small amount) and the nitrogen measured. Nitrogen was passed through the generator to sweep any acid vapors into the water, and the amount of acid determined by titrating against standard alkali. The residue was extracted several times with boiling water and the water evaporated in a platinum basin. The small amount of solid found on evaporation consisted mostly of unchanged ammonium nitrate.

In three closely agreeing experiments carried out as described the following figures were obtained:

1. 2.0079 gms. ammonium nitrate gave 500.5 cc. (corr.) (=0.6286 gms.) free nitrogen, and 0.7352 gms. acid (calculated as nitric).
2. 2.8955 gms. ammonium nitrate gave 635.6 cc. (corr.) (=0.7983 gms.) free nitrogen and 0.9998 gms. acid.
3. 3.8527 gms. ammonium nitrate gave 820 cc. (corr.) (=1.025 gms.) free nitrogen and 1.1000 gms. acid.

In these experiments the average ratio of free nitrogen to acid is 1:1.15. This ratio approaches very nearly to that for two molecules of nitrogen to one of the acid, viz., 1:1.125. The equation which best corresponds to this ratio is as follows:



Reiset and Mellon have shown (*Journ. für Practische Chemie*, 29-365) that when ammonium nitrate is mixed with platinum sponge and heated, decomposition begins at 160° and that the products are nitrogen and nitric acid. The equation by which they express the reaction is identical with that given above. It is unlikely that the platinum enters into the reaction, though it is stated that an insoluble platinum compound is produced. I have not been able to confirm this latter statement. If the platinum does not enter into the reaction, but acts as a true contact agent, then there seems no reason for believing that the manganese dioxide, in this reaction at least, acts in a chemical way.

It is possible that an intermediate product containing manganese may be isolated; and this will be the object of further research.